PATENT SPECIFICATION

DRAWINGS ATTACHED

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1,182,407

1,182,407

Date of Application and filing Complete Specification: 17 Oct., 1968.

No. 49343/68.

Complete Specification Published: 25 Feb., 1970.

Index at acceptance: —C7 F(1B2, 2F, 4K)

International Classification: —C 23 c 11/04

COMPLETE SPECIFICATION

A Method of and a Device for Diffusion Chromium Coating of Metal Articles

We, TSENTRALNY NAUCHNO - ISSLEDOVATELSKY INSTITUT TEKHNOLOGII MASHINOSTROENIA, of Sharikopodshipnikovskaya ulitsa 4, Moscow, Union of Soviet Socialist Republics, a Corporation organised and existing under the Laws of the Union of Soviet Socialist Republics, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THE PRESENT INVENTION relates to the chromium coating of metal articles employed in machine-building, mainly such articles made of iron or of its alloys.

Several industrial methods of diffusion chromium coatings are known in the art.

The most widely applied method (due to its simplicity) consists in that the articles to be chromium coated are enclosed, together with a powdered coating mixture, in metal containers provided with fusible seals. Then the containers are heated in conventional furnaces. Upon cooling the containers, tapping the fusible seal and taking out the articles, the latter, if necessary, may be heat-treated (i.e. hardened and then tempered).

The disadvantages of this and similar methods reside in the fact that they are highly labour-consuming and are of low production efficiency, this being due to the employment of powdered materials, hence they are inapplicable to mass-production.

Another method has been found some application, according to which the articles to be treated are brought into contact with pieces of specially prepared refractories within a fixed airtight retort of a bell- or shaft-type furnace, the atmosphere required for chromium coating being provided inside by using a mixture of hydrogen and hydrogen chloride. The low-porosity refractory material used is previously saturated with chromium chloride vapour in the same retort.

Another method is known, whereby the articles to be chromium coated are isolated from the chromium-containing material, and, to provide the atmosphere required for chromium coating, ammonium fluoride and hydrogen are used.

The latter two methods, however, suffer from the following principal disadvantages: the use of explosive and noxious gases such as hydrogen, hydrogen chloride and hydrogen fluoride, and low production efficiency inadequate for mass production.

A further method has been employed whereby the treated articles are likewise not in contact with the chromium-containing material which is in the form of solid particles, while diffusion chromium coating is effected in an atmosphere of chromium chlorides and hydrogen. This method is applicable to both sheet materials (in a bell-type furnace with a blower fan) and small-sized articles (in a furnace with a rotary retort) with immediate heat-treatment thereof.

The disadvantages inherent in this method, as far as they are described in the relevant literature, are as follows: a reduced degree of saturation of the treated surfaces with chromium and the employment of hydrogen.

One further method of diffusion chromium coating of articles is now in current practice, whereby the chromium coating process is effected inside a fixed retort by contact between the articles being treated and granules

[*Price 5s. 0d.*]

of a chromium-containing material in an atmosphere of hydrogen whose inflow is stopped before heating. Hydrogen chloride necessary for a chromium coating atmosphere is formed on heating of chloride which is introduced into the retort along with the articles to be chromium coated and the chromium-containing material. The method in question eliminates the use of not only powdered substances (i.e. chromium and alumina) but also noxious gases, while the gas outlet pipe is not clogged with solid reaction products (i.e. iron chloride).

The disadvantages from which this method suffers are: the use of hydrogen, which is liable to explode; the possibility of the granules of chromium-containing material caking at high temperatures and sticking to the surface of the articles being treated; and low production efficiency stemming from a necessity to reheat the articles for their final heat treatment.

Thus, the principal disadvantages inherent in all the methods of diffusion chromium coating which are used currently, are as follows: the employment of powdered materials; low production efficiency; use of explosive and noxious gases; and, sometimes, inadequate degree of saturation with chromium of the surfaces to be treated.

The invention consists in a method of diffusion chromium coating of articles made of iron or of its alloys, whereby the chromium coating process proceeds in a reducing hydrogen-containing atmosphere, with the aid of a halogen or halide, inside a heated retort into which are charged the articles to be chromium coated and a chromium-containing material, substantially in granular form, and upon completing the chromium coating process the chromium-containing material is separated from the articles being chromium coated while hot and is placed in a separate chamber, in which it is protected against being oxidized or cooled, and after the chromium coated articles have been discharged from the retort and a fresh charge of articles has been charged, said chromium-containing material is recharged into the chromium coating chamber.

To create a reducing atmosphere, hydrocarbon gas may be introduced into a space within the retort that is closed during heating and holds the articles to be chromium coated at some excess pressure.

It is expedient to utilize the heating of the articles within the retort while being chromium coated for their hardening, by feeding the articles to a quenching bath immediately from the retort.

Halides may be fed into the retort contained in a capsule which is adapted to open under the pressure of the halide vapour developed inside.

The invention also provides apparatus for the diffusion chromium coating of articles made of iron or its alloys, the apparatus comprising an elongated retort which is tiltable about a transverse axis and rotatable about a longitudinal axis, the retort comprising a working chamber and an additional chamber connected in series in the longitudinal direction of the retort by a valve which when open allows chromium containing material to pass from one chamber into the other, and when closed forms a gas-tight seal, the apparatus further comprising ducts opening into the working chamber for blowing gases through the working chamber.

The application of the present invention increases the production efficiency of the process, improves the quality of the chromium coating of articles, cuts down the consumption of the chromium-containing materials used and reduces the hazardousness of the process.

The chemistry of the chromium coating process made use of by the method according to the invention is conventional and proceeds by virtue of transferring atomic chromium to the surface of the article to deposit thereon, this being the result of the following principal reactions:

$$CrCl_2 + Fe \longrightarrow FeCl_2 + Cr \quad (1)$$

$$CrCl_2 + H_2 \longrightarrow 2HCl + Cr \quad (2)$$

$$CrCl_2 \longrightarrow Cr + Cl_2 \quad (3)$$

The formation of hydrogen in the atmosphere inside the retort is mostly due to an equilibrium dissociation of methane when not flowing through the retort.

$$CH_4 \rightleftharpoons 2H_2 + C \quad (4)$$

At a temperature of 900°C the equilibrium hydrogen content in the atmosphere is found to be 98 per cent which ensures a reducing atmosphere and allows reaction (2) to proceed. Carbon produced as a result of reaction (4) combines with chromium to produce carbides to some extent. However, due to side reactions, this does not lead to any appreciable carbonizing of the chromium granules.

In what follows the invention is disclosed in an embodiment thereof given by way of illustration to be taken in conjunction with the accompanying drawings, wherein:—

Figure 1 is a central longitudinal section view of an embodiment of apparatus according to the invention, showing its housing partly broken away; and

Figure 2 is a section taken on the line II—II of Figure 1.

Now referring to Figures 1 and 2, the apparatus comprises a double-chamber retort 1 partitioned into a working chamber 2 and an additional chamber 3 by a water-cooled valve 4 provided with a central bore 5 to

admit hydrocarbon gas to the working chamber 2; a mechanism 6 to turn the retort 1 about the axis a—a; a mechanism 7 to actuate the valve 4; a mechanism 8 to tilt the retort 1 about its transverse axis b—b; and an electric heater 9.

The entire device is accommodated inside a housing 10 and mounted on a bed frame 11.

The working chamber 2 is provided with longitudinal ribs 12 to agitate the charge contained therein when the retort is being rotated, thereby contributing to uniform quality of the articles being treated and preventing the particles of the chromium-containing material from being caked and stuck to the surface of the articles at high temperatures.

The front portion of the retort 1 is provided with a cover or lid 13 in which a shuttable flue 14 is located, employed to blow hydrocarbon gas through the working chamber 2 of the retort 1 *via* the bore 5 in the direction indicated with the arrow "A"; further, said cover or lid accommodates an airtight duct 15 for feeding in ammonium halide or chromium chloride. The appropriate proportions of these salts are charged in a metal capsule which can be introduced into the duct 15 at any point in the chromium coating process and then caused to move into the heated-up extended portion thereof by a spring or other means.

While being sublimed by heating, the above salts evolve vapour whose pressure drives out the metal foil bottom of the capsule so that the halide vapours pass into the working chamber 2 to form the atmosphere required for chromium coating.

The retort 1 keeps rotating about its longitudinal axis a—a on rolls 16 throughout the chromium coating process. To fix the retort 1 in the required position when tilting about its transverse axis b—b, an electro-magnetic brake 17 is provided.

The articles to be chromium coated are charged into the working chamber 2 which has been preliminarily heated up to 850°C, through a charging mouth 18 of the retort 1, with the lid 13 removed and the retort 1 in an approximately vertical position. The granules of chromium-containing material are in the additional chamber 3 at the same or at a lower temperature.

The working chamber 2 of the retort 1 having been blown through with hydrocarbon gas and a reducing atmosphere having built up inside, the retort 1 is inclined with its mouth 18 downwards at 45 to 60° to the horizontal, the valve 4 opened and the chromium-containing material allowed to pour into the working chamber 2 where it is mixed with the articles to be treated.

Once the articles have been heated to a required temperature, ammonium halide or chromium chloride is fed into the working chamber by means of the metal capsule through duct 15.

Then the charge is heated to a temperature of 900 to 920°C and held at that temperature for 2.5 to 4 hours.

On completion of the chromium coating process the chromium-containing material is separated from the chromium coated articles by means of the valve 4 which forms a circular gap when the rotating retort is inclined with its mouth 18 upwards at 15 to 30° to the horizontal. The width of the gap is selected to be less than the size of the articles under treatment but greater than the maximum size of the granules of chromium-containing material.

After the chromium-containing material has been separated, valve 4 is shut off, the articles cooled to a temperature of about 850°C, the lid 13 of the retort 1 opened, the retort 1 inclined with its mouth 18 downwards so as to discharge the finished articles to a quenching tank (not illustrated in the drawing), wherein they are oil-hardened.

Thus, the apparatus for diffusion chromium coating according to the invention allows complete mechanization of the whole process of chromium coating, from the charging of the articles into the retort up to their discharge into the quenching tank.

The herein-disclosed method has the following advantages: increased efficiency of the process as a result of the reduced heating time, since the articles are charged into the preliminarily heated-up retort and are in contact with the heated-up granules of chromium-containing material, and also due to the use of the heating of the articles, while being chromium coated, for their hardening by placing them into the quenching bath immediately from the retort.

The high production efficiency of the present method is by virtue of the high rate of use of the working volume of the retort, amounting to 70—80 per cent.

The weight ratio of the articles to the granules of chromium-containing material, depending upon the area of surface being chromium coated, ranges between 1:5 and 1.3. The amount of chromium in a charge can be reduced and the aforesaid ratio increased if chromium dichloride ($CrCl_2$) is used along with (or instead of) ammonium chloride, on which account the production efficiency can be increased further.

A uniform diffusion chromium coating of the articles throughout the working volume of the retort is obtained by uninterruptedly agitating them with the granules of chromium-containing material.

An economical use of the chromium-containing material is achieved, since it is not discharged from the retort and, consequently, its losses are negligible.

On account of absence of abrupt thermal cycling or temperature drops of the granules of chromium-containing material, its composition varies but slightly, and chromium consumed by the solid diffusion process and inevitable losses, is periodically replenished.

The minimum required consumption of halide is controlled by a proportioned feed thereof into the retort.

The use of hydrocarbon gases such as natural gas or methane, instead of hydrogen and noxious gases, completely eliminates the harmfulness and substantially reduces the explosion risk of the process.

The atmosphere in the retort containing hydrogen, required for chromium coating can rapidly be replaced by an atmosphere with a negligible hydrogen content. Charging of the articles to be treated into the retort and their discharge therefrom can be effected through a gas blanket or curtain. The use of hydrocarbon gas improves the process inasmuch as it makes it unnecessary to utilize a considerable number of bottles containing high-pressure compressed hydrogen.

Moreover, the employment of hydrocarbon gas along with a diluent gas, makes it possible to effect gas case-hardening or carburizing, as well as diffusion chromium coating and hardening of the articles, for a single heat in the device of the invention.

Maximum wear-resistance of the finished articles and the simultaneous imparting of anticorrosive properties is attainable by chromium coating articles made of high-carbon steel or those made of low-carbon steel which have been carburized. Thus, for example, testing of bush-roller chains, the components of whose joints have been case-hardened and then chromium coated, has shown their wear-resistance under service conditions to be six times and under static conditions to be up to ten times as high as the conventional, serially manufactured, non-chromium-coated chains. The joints were made of the following steels: (a) C 0.07—0.14, Si 0.17—0.37, Mn 0.35—0.65, S $\leqslant$0.04, P $\leqslant$0.035, Cr$\leqslant$0.15; (b) C 0.12—0.19, Si $\leqslant$0.07, Mn 0.25—0.59, S $\leqslant$0.04, P $\leqslant$0.04, Cr $\leqslant$0.25; and (c) C 0.17—0.23, Si 0.17—0.37, Mn 0.5—0.8, S $\leqslant$0.035, P $\leqslant$0.035, Cr 0.7—1.0; the proportion of alloying elements being percentage by weight.

WHAT WE CLAIM IS:—

1. A method of diffusion chromium coating of articles made of iron or of its alloys, whereby the chromium coating process proceeds in a reducing hydrogen-containing atmosphere with the aid of a halogen or halides, inside a heated retort into which are charged the articles to be chromium coated and a chromium-containing material, substantially in granular form, characterized in that upon completion of the chromium coating process, the chromium-containing material is separated from the articles while hot, and is placed in a separate chamber in which it is protected against being oxidized or cooled, and after the chromium coated articles have been discharged from the retort and a fresh charge of articles has been charged, said chromium-containing material is recharged into the chromium coating chamber.

2. A method as claimed in claim 1, in which in order to provide the reducing hydrogen-containing atmosphere, a hydrocarbon gas is introduced into a space within the retort which is closed during heating and holds the articles to be chromium coated at some excess pressure.

3. A method as claimed in claim 1 or 2, in which the heating of the articles while being chromium coated inside the retort, is employed for their hardening by feeding said articles into a quenching bath immediately from the retort.

4. A method as claimed in any of claims 1 to 3, in which halides are fed into the retort contained in a capsule which is adapted to open under the pressure of the halide vapour developed inside.

5. Apparatus for the diffusion chromium coating of articles made of iron or its alloys, the apparatus comprising an elongated retort which is tiltable about a transverse axis and rotatable about a longitudinal axis, the retort comprising a working chamber and an additional chamber connected in series in the longitudinal direction of the retort by a valve which when open allows chromium containing material to pass from one chamber into the other and when closed forms a gas-tight seal, the apparatus further comprising ducts opening into the working chamber for blowing gases through the working chamber.

6. Apparatus as claimed in Claim 5, comprising a duct opening into the working chamber for introducing halogens or halides into the working chamber.

7. Apparatus as claimed in Claim 5 or 6, in which the valve comprises an aperture by which the chambers communicate and a valve member movable in the longitudinal direction of the retort for closing the aperture.

8. Apparatus as claimed in Claim 7, in which the valve member is rigid with a rod passing longitudinally through the additional chamber and extending through a gas-tight seal in the end of the additional chamber in a slidable manner.

9. Apparatus as claimed in Claim 8, in which one of the said ducts passes through the rod and the valve member.

10. A method as claimed in claim 1 substantially as described herein.

11. Apparatus for the diffusion chromium coating of articles made of iron or its alloys, substantially as described herein with reference to the accompanying drawings.

12. Articles when chromium coated by a method or device according to any of the preceding claims.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1970.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

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1 SHEET This drawing is a reproduction of the Original on a reduced scale

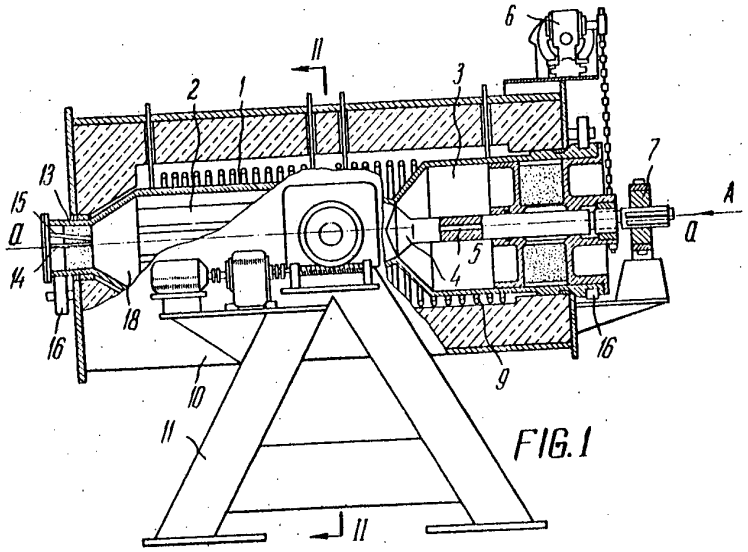

FIG. 1

FIG. 2